

# Factors Affecting the Stability of CdTe/CdS Solar Cells, Deduced from Stress Tests at Elevated Temperature\*\*

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**ToC**      *The stability of CdTe/CdS solar cells appears to be dictated by two distinct mechanisms, viz. excess Cu in CdS, which degrades the photovoltaic junction, and O<sub>2</sub>/H<sub>2</sub>O – induced formation of an insulating oxide at the CdTe back surface contact, creating a barrier for hole transport. This understanding helps to get cells, also Cu-containing ones, that are a priori stable or show self-repair, as shown experimentally.*

**Abstract**      CdTe/CdS solar cells were subjected to heat-stress at 200°C in the dark, under different environments (N<sub>2</sub> and air), and under illumination (N<sub>2</sub>). We postulate that two independent mechanisms can explain degradation phenomena in these cells:

1. *Excessive Cu-doping of CdS* - Accumulation of Cu in the CdS with stress, in the presence of Cl, will increase the photoconductivity of CdS. With limited amounts of Cu in CdS, this does NOT affect the photovoltaic behavior, but explains the crossover of light/ dark current-voltage (J-V) curves. Overdoping of CdS with Cu can be detrimental to cell performance by creating deep acceptor states, acting as recombination centers, and compensating donor states. Under illumination, the barrier to Cu cations at the cell junction is reduced, and, therefore, Cu accumulation in the CdS is enhanced. Recovery of light-stress induced degradation in CdTe/CdS cells in the dark is explained by dissociation of the acceptor defects.
2. *Back contact barrier* - Oxidation of the CdTe back surface in O<sub>2</sub>/H<sub>2</sub>O-containing environment to form an insulating oxide results in a back-contact barrier. This barrier is expressed by a rollover in the J-V curve. Humidity is an important factor in air-induced degradation, as it accelerates the oxide formation.

*Heat treatment in the dark in inert atmosphere can stabilize the cells against certain causes of degradation, by completing the back contact anneal.*

**Keywords:** CdTe/CdS solar cells, Cu-doping, diffusion, heat stress, humidity / Oxygen / O<sub>2</sub>, illumination

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## 1. Introduction

Thin film solar cells made of p-CdTe/n-CdS (schematic structure shown in figure 1) have shown great promise for application as high area - low cost photovoltaic systems,<sup>[1-3]</sup> and cells have exhibited conversion efficiencies as high as 16%.<sup>[4-6]</sup> While some encapsulated CdTe/CdS modules have exhibited encouraging long-term stability in the field and under accelerated stress conditions,<sup>[7, 8]</sup> non-encapsulated CdTe/CdS cells are often unstable under accelerated laboratory stress conditions.<sup>[9]</sup> The extent and type of degradation of the cells can vary with deposition parameters and the nature of stress testing, indicating that more than one degradation mechanism may actually be at work. A frequent feature of degradation in CdTe cells is a drastic increase in cell series resistance ( $R_s$ ) at high forward bias, often termed 'roll-over'. Roll-over is thought to be due to the formation of a barrier for electron transport at the back contact interface, opposing the main cell junction.<sup>[10, 11]</sup> Back contact degradation and increasing  $R_s$  can cause a decrease in fill factor (FF) and short-circuit current density ( $J_{sc}$ ). Other changes in cell characteristics during stress testing (e.g., significant decrease of open-circuit voltage,  $V_{oc}$ ), are suggested to be the result of degradation of the main cell junction.<sup>[9]</sup>

Due to the high work function of p-CdTe, no metal is known which can form an Ohmic back contact to it within the simple Anderson model. However, the addition of small amounts of Cu and other metals to back contact materials (e.g., graphite paste) was found to improve contact properties and initial cell performance.<sup>[12-14]</sup> These additives, and in particular Cu, have generally been thought to be responsible for the low stability of such cells. Cu is considered to be a fast diffuser in CdTe,<sup>[13, 15-17]</sup> and the polycrystalline nature of the CdTe films is thought to assist diffusion via grain boundaries.<sup>[15]</sup> This could lead to poisoning the cell junction by impurities and/ or depletion of the favorable back contact. In a review of the recent literature regarding stability of CdTe/CdS cells, with emphasis on the role of Cu, we proposed a mechanism for the behavior of Cu in CdTe/CdS cells.<sup>[9]</sup> To overcome Cu effects, there has been a recent rise in interest in the search for Cu-free contacts to p-CdTe.<sup>[18-22]</sup>

In the work presented here we have used a combination of analytical methods to test thermally stressed cells to understand the degradation phenomena and correlate them with the distribution and behavior of impurities (especially metals from the back contact) within the cell structures. Preliminary results of this work were reported previously.<sup>[23, 24]</sup> They showed that cell performance can be unaffected during thermal stressing in a dry-N<sub>2</sub> atmosphere, leading us to propose that Cu-containing cells can be stable and that Cu as such is NOT initially a dominant factor in common degradation modes of CdTe/CdS cells. We do note, however, that cells and modules in field studies rarely experience temperatures exceeding 70°C, and that testing at higher temperatures, as done here, could

introduce failure mechanisms that may not normally occur in devices in the field. However, accelerated (or high temperature) stress testing is useful both for further understanding the behavior of CdTe/CdS solar cells and to emphasize potential chemical changes in such cells.

In this full report we also include the effects of illumination during stress and the effect of the presence of O<sub>2</sub>/H<sub>2</sub>O in the stress-atmosphere. Both factors are known to enhance cell degradation (see <sup>[9]</sup> and references therein), and we present models that explain the observed behavior. Chemical and electrical characterizations are used to correlate the degradation with behavior of cell impurities and changes in back contact chemistry. In addition, we present data showing that cells that had degraded during light stress were found to recover their original performance after some time. Finally, we will show that cells can be stabilized against light-induced degradation, and degradation during cell storage at room ambient, by heating in the dark in an inert atmosphere.

## 2. Results

### 2.1. Stressing in dry N<sub>2</sub> in the dark

We have recently shown <sup>[23, 24]</sup> that CdTe/CdS cells generally show very little or no degradation with thermal stress at 200°C in dry-N<sub>2</sub> atmosphere in the dark for >50 hrs (Figure 2). In about 50% of the cells stressed in dry-N<sub>2</sub> in the dark, a small degree of degradation occurred (efficiency decreased by 10-20% of its initial value), due to slight decreases in FF or  $J_{sc}$ . However, rollover was never observed, even with increasing stress time. In all cells measured, the dark current density-voltage (J-V) curves show an increase in dark  $R_s$  with increasing stress times, and, hence, a significant increase in light-dark J-V crossover (Figure 2). Such behavior is generally associated with increasing cell photoconductivity.

#### *Laser Beam Induced Current (LBIC)*

LBIC measurements obtained from contacted and non-stressed cells show a bright (high current), reasonably homogeneous image (for example, see Fig. 8a below). Some dark (low current) patches are observed, as we previously showed <sup>[24]</sup>, which agree with high-resolution Apparent Quantum Efficiency data.<sup>[25]</sup> These are likely due to areas of poor contact and/ or mechanical damage. Thermal stressing over 40-50 hrs in the dark in dry-N<sub>2</sub> had no effect on the LBIC image of the cell, in sharp contrast to effects of air stress (see later).

#### *Secondary Ion Mass Spectroscopy (SIMS)*

To monitor the role of diffusion and behavior of impurities in the cells with stress, a series of SIMS and photoluminescence (PL) experiments was carried out (see also <sup>[23, 24]</sup>). Fig. 3 shows the SIMS profile of a number of elements from a non-stressed cell and from a piece of non-contacted CdTe/CdS substrate. The positions of the CdS/CdTe and CdS/transparent conductive oxide (TCO) interfaces can be deduced

from the Te, S and Sn profiles. The non-contacted cell shows a low amount of Cu in the CdTe ( $1 \times 10^{17}$  Cu atoms/cm<sup>3</sup>), with a higher level observed in the CdS layer ( $9 \times 10^{19}$  Cu atoms/cm<sup>3</sup>). This means that Cu is present in the cell in significant amounts even prior to contacting, probably originating from impurities in the starting materials, chemicals and equipment used for After contacting, with Cu-containing graphite paste (see in the Experimental section), the most notable feature is the accumulation of Cu in the CdS layer of the cell. The importance of this accumulation (which was already apparent in earlier experimental data<sup>[27, 28]</sup>) has been discussed by us elsewhere.<sup>[9, 23]</sup> The Cu concentration increases to  $1.5 \times 10^{20}$  atom/cm<sup>3</sup> in the CdS, compared to  $3 \times 10^{18}$  atom/cm<sup>3</sup> in the CdTe. No increase in Cu levels was observed, from SIMS measurements, in regions that were not below the back contact. Previously, we have compared behavior of Cu in cells to its behavior in CdTe/TCO/glass (CdS-free) structures contacted with Cu/HgTe/C<sup>[23]</sup>. No accumulation profile of Cu was observed in these structures. However, the level of Cu in CdTe increased dramatically and exhibited a U-shaped profile ( $7.5 \times 10^{18}$  Cu atoms/cm<sup>3</sup> at the CdTe/ITO interface), similar to that expected for a system where the diffuser is reflected at a diffusion barrier.<sup>[29]</sup> These results clearly highlight that Cu exhibits a high affinity for polycrystalline-CdS, and that it diffuses rapidly throughout the cell structure into the CdS layer. The accumulation of Cu in CdS was corroborated by the results from Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) experiments (not shown).

Fig. 3 also shows the SIMS profile of a CdTe/CdS cell following 15h stress in a dry N<sub>2</sub> atmosphere. Although no significant change in the Cu level in the CdTe layer is observed with such stress, the Cu level in the CdS layer slightly increased (to  $2.0 - 3.5 \times 10^{20}$  Cu atoms/cm<sup>3</sup>). The Cu content of the CdS layer could be increased further by longer stress time. Similar Cu profiles were measured in cells stressed in air. This observation indicates that heat accelerates Cu diffusion through the CdTe/CdS structure, and that this process is not affected by the stress atmosphere. Some accumulation of Cl in the CdS is always present, however, the amount of Cl detected in the different cells varied and showed no clear pattern with stress history. The profiles of Cd, Te, S and Sn did not change significantly with contacting or stress.

Ag (originating from the contact metallization) penetrates in a manner similar to that observed for Cu, with accumulation in the CdS and at the CdS interfaces. No difference was found in Ag content between non-stressed and dark N<sub>2</sub>-stressed cells. Small amounts of Au were found after stressing close to the CdTe back contact in Au-metalized cells, indicating its slower diffusion in CdTe. As generally no degradation was noted in cells stressed in the dark in dry N<sub>2</sub>, Ag and Au are probably not involved in degradation processes.

cell manufacture (as was seen also by Durose et al.<sup>[26]</sup>). Accumulation of Cl, presumably originating from the CdCl<sub>2</sub> treatment, is observed in the CdS layer (e.g.  $1 \times 10^{20}$  Cl atoms/cm<sup>3</sup> compared to  $1 \times 10^{19}$  Cl atoms/cm<sup>3</sup> in the CdTe layer).

SIMS was also carried out on the CdS layer from cells following stress treatments, in order to eliminate the possibility that measurement artifacts led to the observed Cu accumulation in CdS. The samples were prepared by removing the Cu contact and the CdTe layer, as described in the experimental section. The results (not shown) showed that, merely applying the Cu-containing back contact to the cells led to a significant increase in Cu content in the CdS. With dark stressing, irrespective of atmosphere, the level of Cu through the bulk of the CdS layer did not change, but a significant accumulation of Cu was observed at the CdS/ITO interface. The amount of Cu accumulated at this interface increased with longer stress times.

**PL** PL experiments were carried out to monitor the electronic behavior of Cu that accumulated in the CdS (see also in<sup>[23, 24]</sup>). Near-identical PL results were obtained from the CdS layers in complete cells, illuminated through the glass, and from CdS layers after the removal of CdTe, indicating that the FeCl<sub>3</sub>(aq) etch treatment (to remove CdTe) does not affect the Cu content of the CdS layer.

Fig. 4 shows PL data of CdS layers from cell structures that had received various treatments. The spectrum obtained from a non-contacted substrate shows two bands at 680 and 750 nm. The 680 nm band is assigned to a Cl<sub>s</sub>-V<sub>Cd</sub> type complex.<sup>[30]</sup> With contacting the intensity of the 680 nm band decreases and the 750 nm band now appears to shift to longer wavelengths. With stress in dry N<sub>2</sub> (and air – see later) in the dark over 16 h, the intensity of the 680 nm peak decreases further and a new peak is found at 790 nm. The peak at 790 nm can be assigned to the formation of a Cu<sub>Cd</sub>-related transition.<sup>[31]</sup> With longer stress, the 680 nm transition continues to decrease in intensity with respect to the 790 nm band. These changes are only observed from CdS that was situated physically below the back contact (as was the case for Cu accumulation, cf. SIMS results, above). Sampling CdS from a region outside the back contact area gave spectra near identical to those obtained for a non-contacted substrate (not shown), irrespective of stress atmosphere and stress time. No features consistent with changing cell history could be detected in the IR region (>800 nm) of the PL spectra of CdS layers of CdCl<sub>2</sub>-treated cells.

**The effect of Cl** To investigate the effect of Cl, a series of cells was prepared from substrates that had not received CdCl<sub>2</sub> treatment. As expected, the resultant cells were of poor quality (efficiencies of 2–3.5 %). The poor quality of cells made analysis of cell performance difficult. Still, such cells, whether stressed in air or in dry-N<sub>2</sub> (~40-50 hours), did exhibit degradation, mainly due to a decrease in V<sub>OC</sub> (from

~800 mV to ~650 mV), but did not show rollover at forward bias. As with standard cells the dark series resistance increased with stressing.

SIMS analysis of these untreated (non-contacted) substrates showed low levels of Cl ( $\sim 2 \times 10^{17}$  Cl atoms/cm<sup>3</sup>) throughout the cell, and possibly some accumulation in the CdS layer. The origin of the Cl is probably the commercial TCO layer, as an impurity left from the manufacturing process. Due to a high level of Cl in the TCO layer, estimating the low Cl concentration in CdS was difficult. The Cl level in the CdTe did not vary with contacting or stress. However, the Cu profiles showed the same trend as in standard CdCl<sub>2</sub>-treated cells, with higher levels of Cu in the CdS layer. The Cu quantities are generally similar to those measured in CdCl<sub>2</sub>-treated cells. Unlike the standard cells, though, the maximum of the Cu accumulation peak appears to be located at the CdS/CdTe interface. Following stressing, the profiles obtained became similar to those of standard cells with Cu accumulation throughout the whole CdS region. As these cell structures did not receive CdCl<sub>2</sub> treatment, the extent of CdTe/CdS intermixing is expected to be less than for standard substrates. Therefore, we can assume that immediately after contacting Cu accumulates at the CdTe side of the CdTe/CdS interface. With stressing this interface becomes further intermixed and Cu now diffuses through the entire CdS layer.

The CdS PL spectra of these cells prior to contacting were very different from those obtained with CdCl<sub>2</sub>-treated cells. Only weak peaks at ~600 and 640 nm and a very weak and broad band centered at ~760 nm were present in this spectrum. However, unlike CdCl<sub>2</sub>-treated samples, in this case no change was observed in the PL spectra upon contacting, while, with stress in the dark (over 42 hours) a new and very intense band at 790 nm was formed. These observations correlate with the SIMS results for non-CdCl<sub>2</sub> treated cells, showing little initial Cu accumulation in the CdS and, thus, little doping (as judged from the PL) of the CdS layer following contacting. Only with stress do the CdS layers become doped by Cu (and form Cu<sub>Cd</sub> complexes according to our interpretation). This points to the involvement of Cl in doping of CdS.

## 2. 2. Stressing in dry N<sub>2</sub> in light

Stressing at 200°C in N<sub>2</sub> under illumination at open circuit ("light stress") was found to cause cell degradation. While cell degradation characteristics varied, the degree of degradation was generally less for good cells (initial efficiency > 9%, degradation decreased the efficiency by 10-20% of the initial value) and greater for initially poorer cells (up to 50% loss in efficiency). The FF was the cell parameter that showed, on the average, the greatest change. The drop in efficiency and FF occurs gradually during ca. 50 h stress (in contrast to air-stressed cells, which degrade initially relatively rapidly), and stops at longer times. V<sub>OC</sub> shows initially a slight increase, and then a gradual drop, while J<sub>SC</sub> drops at first and then

stabilizes. Some rollover was noted in about half of the cells following stressing under illumination.

## SIMS

Cu content was found to be higher in light-stressed than in dark (N<sub>2</sub>) stressed cells (with similar stress times) in all parts of the cell, but most significantly in the CdS. This may indicate that light-induced degradation is related to enhanced Cu indiffusion. The Ag concentration was slightly higher in cells stressed in light than in dark, in dry N<sub>2</sub>, but only in the CdTe. As Ag is expected to act as an acceptor in CdTe, it should not be involved in degradation. No difference in Au content in the cell was noted between dark- and light-stressed cells.

## Recovery and Stabilization

Some cells that had degraded during light stress (in dry N<sub>2</sub>) were found to recover their original performance after some time (in the order of days), either under ambient conditions or by heat treatment at 200°C in dry N<sub>2</sub> in the dark. However, this was only seen for cells that had been stressed for short times (~20 hr), and not for cells that had received longer stress treatments (> 60 hr). This indicates that reversible electronic and/or chemical changes occur in the cell structure at shorter times, which then become irreversible after longer stress times.

Several cells received heat treatment in dry N<sub>2</sub> in the dark, prior to being stressed under illumination. Cells that did not exhibit any degradation during the initial heat treatment were stable and did not show any degradation with subsequent light-stress (Figure 5), unlike cells that did not receive heat treatment in the dark prior to light-stressing (see above). Therefore, heating in the dark, in a dry, inert atmosphere, stabilized these cells.

Cells that degraded during heat treatment prior to light stressing showed some improvement in performance (up to 50% recovery of the efficiency loss) during the light stress, mainly due to an increase in J<sub>SC</sub> and V<sub>OC</sub>. This was accompanied by a decrease in dark R<sub>S</sub>, leading to a lower degree of light-dark J-V crossover, presumably due to a decrease in cell photoconductivity.

## 2. 3. Stressing in air in the dark

All CdTe/CdS cells that were stressed in ambient air at 200°C in the dark degraded substantially. The most noted feature of degradation in the J-V characteristics is the formation of roll-over following ~20 hours of air stress, which results in a significant decrease in FF, accompanied by a decrease in the J<sub>SC</sub>, and a smaller drop in V<sub>OC</sub> (Figure 6). The dark J-V curves of the same cells show an increase in series resistance, and hence a stronger light-dark J-V crossover, which correlates with the appearance of rollover in the illuminated plots. The resistance continues to increase with further stress.

Degradation in air-stress occurs initially relatively fast. After further stressing ( $\geq 20$  h) there is some improvement of the FF and the  $V_{OC}$ , followed by further, slow degradation upon continued stress.  $J_{SC}$  remains low after the initial drop. Higher efficiency cells degrade more than lower efficiency cells, i.e., there is a smaller variation in cell parameters of different cells after degradation than before. No difference was found in the Cu distribution within the cell (as measured by SIMS) between cells stressed in the dark in air and in dry  $N_2$ . In air-stressed cells the Ag content throughout the cell (as measured by SIMS) is higher than in the unstressed and dark- $N_2$  stressed samples, suggesting oxide-assisted in-diffusion, or grain surface adherence. However, no difference was found between Ag- and Au-metallized cells in terms of degradation, and no change in Au content was seen between air-stressed and unstressed cells. This suggests that, as was noted above for Cu, Ag in-diffusion is not a dominant factor for cell degradation.

*The effect of humidity* When thermal stress was carried out in the dark in a dry air atmosphere ( $> 80$  hours) the extent of the resulting rollover was significantly less than that obtained after stress in room ambient. In a humid  $N_2$  atmosphere rollover formed in the J-V characteristics within 24h of stressing, along with decreases in  $V_{OC}$ ,  $J_{SC}$  and FF, but overall cell degradation was still smaller than that observed for ambient air-stressing. When stressing was carried out in humid air, more pronounced degradation occurred, with a greater degree of rollover than in the other cases. These observations agree with our finding that after unstressed cells are stored in room ambient (humid conditions), they show small drops in all J-V parameters after several days, with the FF generally exhibiting the greatest decrease. J-V characterization showed that this drop was due to a slightly increased resistivity (no rollover was observed under these conditions). If the unstressed cells were stored in a vacuum desiccator then no decrease in performance was observed, but rather an increase, mainly due to a change in short circuit current.

*Stabilization* Cells that were stable under dark stressing in dry  $N_2$  were also found to be stable against subsequent degradation during ambient storage, unlike cells that were stored in room ambient immediately after contacting (see above). Thus, as noted above for cells stressed in dry  $N_2$  in light, also here cells appear to be stabilized by heat treatment in a dry inert atmosphere in the dark.

*The effect of re-contacting* Re-contacting of air-stressed cells (which had degraded by showing J-V rollover) was investigated to check in how far rollover can be ascribed to contact degradation. The graphite back-contacts were removed and new HgTe/Cu/CdTe contacts were deposited and annealed in the standard way (see in the experimental section). Re-contacting without first etching the exposed CdTe surface showed no change in cell J-V performance and in rollover. However, if the CdTe was etched prior to re-

contacting, the J-V characteristics were improved, as expressed by a significant decrease in the J-V rollover (Figure 7). Short  $Br_2$ /ethylene glycol etches ( $\sim 10$ s) almost completely removed the rollover. Longer  $Br_2$ /methanol etches ( $\sim 30$ s) also resulted in a decrease of the rollover characteristic, but never to the extent observed for  $Br_2$ /ethylene glycol. The difference between the etch solutions is in the solvent viscosity, with the ethylene glycol solution being a slower etchant due to its higher viscosity. As such there was less danger that it etched the Cu-tellurides, that are postulated to be beneficial for the contact (see below).

*LBIC* Changes in cell properties after stressing in air were also monitored using LBIC. Figure 8 shows LBIC images of a cell recorded following 0, 18 and 35 hours air stress. Prior to stress the LBIC image is bright and reasonably homogeneous and, at that stage, the dark (low current) areas are due to regions of poor contact or mechanical damage. With stressing, an increase in the frequency of dark areas along with a decrease in the overall image contrast is observed, indicating a loss of current in localized areas (or loss of contact quality) and a decrease in current over the whole sample area. Smaller LBIC changes from pre-stress measurements were observed for cells stressed in  $N_2$  in the dark. Possible reasons for the loss in current may be electronic (as in the case of light-induced degradation) and/or mechanical (i.e., loss of contact between the CdTe and carbon).

*XPS* Since both the roll-over in J-V curves and the changes in LBIC after air-stressing can be explained by a barrier for the photocurrent at the back contact, we used XPS to characterize changes in the CdTe back surface chemistry after stressing. In these experiments, unstressed cells and cells stressed in the dark in dry  $N_2$  (stable) and in air (degraded) were compared.

Figure 9 shows the XPS Te 3d 5/2 region spectra of the CdTe surface from under the back contacts of (a) air-stressed, (b)  $N_2$  stressed and (c) unstressed cells. The CdTe Te peak in each spectrum is accompanied by an additional Te peak at a higher binding energy (BE), corresponding to oxidized Te. The separation in BEs is  $3.7 \pm 0.1$  eV, suggesting the presence of  $TeO_2$  or  $CdTeO_3$  on the surface (before sputtering).<sup>[32, 33]</sup> The intensities of the Te(oxide)-related peak in the non-stressed and  $N_2$ -stressed samples are much smaller (about one third) than in air-stressed ones. After a short sputtering the separation between the Te BEs decreases ( $3.2 \pm 0.1$  eV). These results suggest the presence of  $CdTeO_3$  or  $CdTe_2O_5$  in the air stressed sample after sputtering,<sup>[33]</sup> and no Te oxides in the non-stressed and  $N_2$ -stressed samples after sputtering. It is very difficult to identify CdO using XPS, as there is almost no shift in the Cd BE between CdTe and CdO.<sup>[34]</sup> One way to estimate the presence of CdO is to deconvolute the O 1s peak, and compare also the amounts of Cd and Te (taking into account preferential sputtering<sup>[32]</sup>). The deconvolution of the O 1s peak was carried out following subtraction of the background using the Shirley

method (cf. <sup>[34]</sup>) and using the following BEs (assuming 285 eV for the Cl<sub>1s</sub> peak): CdO – 529.2 eV, or in its hydrated form Cd(OH)<sub>2</sub> – 531.6 eV, TeO<sub>2</sub> or CdTeO<sub>3</sub> – 530.2 eV, and adsorbed H<sub>2</sub>O – 533.2 eV.<sup>[34-36]</sup> Deconvolution of the O 1s peak confirmed the presence and the relative quantities of Te-oxides. It revealed (together with excess quantities of Cd, even before sputtering) the presence of Cd oxides very close to the surface in all cells measured. The quantities of these oxides are larger by a factor of 2 in the air-stressed cells than in the non-stressed and N<sub>2</sub>-stressed ones.

Comparing the composition of the CdS surface (after removal of the CdTe) after various stress treatments of these cells was somewhat problematic. The CdTe was removed by chemical etch (see in the Experimental section). It was impossible to determine if etching stopped in all samples exactly at the CdTe/CdS interface, because of intermixing (see <sup>[9]</sup> and references therein), layer roughness and the chemical reactivity of the etchant towards CdS (even though CdS reacts much slower than CdTe). Deconvolution of the O 1s peak and the presence of excess Cd suggested the presence of CdO and CdSO<sub>4</sub> in all samples, with no clear differences in quantities between them.

### 3. Discussion

#### 3. 1. Cu-doping

The apparent stability of CdTe/CdS cells under thermal stress in dry N<sub>2</sub> in the dark suggests that stability may depend on the stress atmosphere. From the SIMS and PL results, diffusion of Cu and other impurities does not appear to play a significant role in the initial stages of cell degradation. However, this does not mean that Cu remains inactive within the cell structure, and the role of Cu still must be considered with respect to effects of excessive Cu doping.

Both the SIMS and PL results highlight the very fast diffusion of Cu in the polycrystalline cell structure (probably as Cu<sup>+</sup> in this environment). SIMS shows a 30-40 times increase in the level of Cu in both the CdTe and CdS layers following just the contacting process. The PL spectrum of the CdS layer from a contacted, unstressed cell shows significant changes compared to spectra obtained from a non-contacted substrate. The changes in the spectrum can be assigned to effects of Cu ions diffusing into the bulk of the CdS grains, forming Cl<sub>S</sub>-Cu<sub>Cd</sub> complexes and Cu<sub>Cd</sub> centers at the expense of Cl<sub>S</sub>-V<sub>Cd</sub> complexes. From measurements of cells with no CdCl<sub>2</sub> treatment, it is clear that Cl affects Cu diffusion and doping of CdS, most notably during contact formation. The presence of Cl in the CdS may accelerate the rate of Cu doping of the CdS layer, as Cu<sub>Cd</sub> is known to complex with Cl<sub>S</sub> in CdS, which leads to increased co-solubility of Cu and Cl.<sup>[37]</sup>

For all cells the amount of Cu and extent of Cu doping in the CdS increases significantly with stress, while

there is less change in the level of Cu in the CdTe. The PL results show a decrease in the intensity of the Cl<sub>S</sub>-V<sub>Cd</sub> transition with increasing intensity of the transition ascribed to the Cu<sub>Cd</sub> complex. We note, from PL and SIMS, that the effects of contacting (and stress) are limited to areas of the CdS layers directly below the cell back contact. This indicates that the observed changes are due to the back-contact components, and not to changes in the CdS induced by the stress conditions. The high affinity of Cu for polycrystalline CdS (compared to polycrystalline CdTe) was previously ascribed to the greater chemical stability of Cu-S bonds over Cu-Te bonds as a possible driving force (see <sup>[9]</sup>).

Cl also appears to play an important role during stress. A significant concentration of Cl is detected in all samples. SIMS showed that Cl also exhibits an accumulation profile through the CdS layer, which was confirmed by the presence of Cl-related complexes from PL measurements. By comparison with cells that were not CdCl<sub>2</sub>-treated, we concluded that Cl enhances Cu diffusion into CdS, and is involved, with Cu, in co-doping of CdS (see above). Recrystallization of CdS in the presence of Cu and Cl is traditionally a method for the preparation of photoconducting CdS (cf., e.g., <sup>[38]</sup>). Thus, stressing of cells with significant concentrations of Cu and Cl in the CdS layers is expected to increase photoconductivity of the cells. We have previously considered possible effects of increasing CdS photoconductivity on device behavior and stability (see <sup>[9]</sup> and references therein, for discussion). Increasing photoconductivity of CdS (or other cell components), and hence increased dark resistivity of the material, will not affect the illuminated J-V curve of a device, as long as the resistivity under illumination remains low enough. Increased dark resistivity will be easily observed by a decrease in the slope of the dark J-V curve (increasing R<sub>s</sub>) at forward bias, which will lead to a significant increase in the degree of light-dark J-V crossover (as observed in this study; cf. Figure 2). We propose that this photoconductivity may also be related to stability during stress in the dark, by way of complexes of Cl- and Cu-related defects in the CdS, possibly [Cu<sub>Cd</sub>Cl<sub>S</sub>].<sup>[37]</sup> This complex may prevent Cu from acting as a deep trap in CdS,<sup>[38]</sup> assuming the Cu concentration in the CdS is lower or of the same order of magnitude as the Cl concentration (as is the case in contacted and dark-stressed cells measured by SIMS in this study, see above).

SIMS and PL results both indicate the same Cu behavior, regardless of the atmosphere or humidity present during stress testing in the dark. Therefore, the cell (in)stability observed with thermal stress in air or humid conditions cannot be the direct result of Cu diffusion or Cu doping in the cell. Instead, our results suggest that it is the result of the action of atmospheric components on the back contact interface and/or the main cell junction. However, during light-stress excessive Cu-doping is expected to cause degradation.

*Light effects* The acceleration of cell degradation by illumination during stress at open circuit is well

known.<sup>[39-41]</sup> This behavior may be explained in a manner similar to that used to explain the effect of forward-bias stressing, i.e., as the result of lowering the electrostatic barrier to  $\text{Cu}^+$  ion drift at the cell junction, and the subsequent Cu accumulation in the CdS. The built-in voltage at the heterojunction slows the concentration gradient-driven diffusion towards the CdS, while forward bias and/or light lowers that barrier for diffusion.<sup>[9]</sup> Cu accumulation in the CdS was also observed in stable cells, stressed in the dark in dry  $\text{N}_2$ . However, excess Cu quantities, as shown by SIMS, may create deep acceptor states, which can act as recombination centers and decrease the effective donor concentration of the CdS (see ref. <sup>[42]</sup> for discussion). Enhanced Cu diffusion into the CdS can be correlated with Cu depletion at the back contact, giving rise to the formation of a barrier for current transport. This can explain the small rollover seen in some of the light-stressed cells.

Recovery (partial or full) of light-stress induced degradation in CdTe/CdS cells by storage or anneal in the dark has been observed previously,<sup>[43-45]</sup> as was reversibility of bias stressing effects by application of the opposite bias.<sup>[46, 47]</sup> A number of explanations can be forwarded for this:

- Dissociation of the acceptor defects in CdS (for example  $\text{Cu}_{\text{Cd}}$  and  $[\text{V}_{\text{Cd}}\text{-Cu}_i]$  dissociating into  $\text{V}_{\text{Cd}}^+$   $\text{Cu}_i^-$ ), and back-diffusion of  $\text{Cu}^+$  driven by a concentration gradient and the restored junction field (either during later heating or during aging in the dark) can account for the restoration of the original behavior of the light-degraded cells. Transient shallow acceptor states are known to be present in Cu-doped CdS under illumination.<sup>[48]</sup>
- Another possible mechanism, suggested by Grecu et al.,<sup>[45]</sup> is the reversible reduction in carrier concentration in CdTe, if stressed under illumination. However, Grecu et al.<sup>[45]</sup> showed that while the carrier concentration could be restored by heat treatment in the dark, storage at room temperature reduced the carrier concentration, suggesting that the mechanism acting in our cells is different.

Reversibility of the effects of stress under bias by application of the opposite bias supports the explanation of Cu-ion diffusion in the cell structure. The effects of Cu diffusion on CdS PL were more stable with time than those on CdTe PL.<sup>[49]</sup> However, it remains to investigate the longevity of the effect of Cu diffusion on CdS:Cl. The lack of reversibility in cells stressed for longer times implies that the concentration of Cu involved in the processes that lead to degradation is crucial, i.e., beyond a certain Cu threshold the system can no longer repair itself (by back diffusion/drift).

Heat treatment in the dark, prior to light stressing, stabilizes the cells. A possible reason is that such treatment prevents the formation of deep Cu states. This can be explained by the elimination of Cd vacancies, which are necessary for the formation of

acceptor states. Alternatively, we can suggest that the standard contact anneal is too short, and is completed during the extra heat treatment. In that way sufficient Cu and Te (present after etching) are converted to the relatively more stable Cu-rich  $\text{Cu}_{2-x}\text{Te}$  (with very narrow range of existence,  $x=0.015\text{-}0.026$  <sup>[50]</sup>), which is known to form at the back contact/ CdTe interface of high-efficiency cells.<sup>[51]</sup> As a result, the release of Cu ions from the  $\text{Cu}_{2-x}\text{Te}$ ,<sup>[52]</sup> which is expected to be slower than that from Te-rich Cu-tellurides (due to their larger range of existence), is the only source for Cu diffusion, and, hence, cell degradation is noticeably attenuated. Further chemical analysis of the stabilized vs. degraded cells would be valuable to strengthen this explanation. A similar argument may also explain the differences in stability between good quality and poorer cells, as a higher degree of conversion of Cu and Te to  $\text{Cu}_{2-x}\text{Te}$  was found in higher efficiency cells.<sup>[51]</sup>

The partial recovery in the light, of cells that degraded during stressing in the dark in dry  $\text{N}_2$ , correlates with the initial increase in  $V_{\text{OC}}$  during light stressing. Such initial increase in  $V_{\text{OC}}$  was also observed by Sasala et al. <sup>[53]</sup>, who explained it by the emptying of traps in the CdTe near the junction.

### 3. 2. Air/ $\text{H}_2\text{O}$ effects

The adverse effect of air during stressing has been noted previously.<sup>[40, 54]</sup> Our results provide clear experimental proof for an air-induced degradation mechanism. This mechanism is not operative in cells that are stressed in a dry inert atmosphere in the dark. The cause of this mechanism should not be sought in Cu redistribution as no significant differences are found for Cu distribution throughout both air-stressed and  $\text{N}_2$ -stressed cells.

Our observations that etching and re-contacting removes the rollover are similar to those of Hegedus et al. <sup>[52]</sup> and suggest that the formation of J-V rollover is the result of changes at the back contact interface. The observation that etching prior to re-contacting is essential to restore the original cell properties points to the need to remove a surface layer that is detrimental to the cell function. XPS measurements show significantly higher quantities of Te-oxides, as well as of Cd-oxides, in the air-stressed cell than in the non-stressed and  $\text{N}_2$ -stressed cells. We postulate that oxygen migration through the back contact and the resulting formation of an insulating oxide layer on the CdTe surface is the main reason for degradation of unencapsulated cells in air, in agreement with earlier works.<sup>[39, 54]</sup>  $\text{CdTeO}_3$ , the stable thermal oxide of CdTe (also found on the CdTe back surface of cells <sup>[39]</sup>), decreases the hole current from p-CdTe in a p-CdTe-oxide-metal junction.<sup>[55]</sup> Wang et al. explained this by a lower tunneling probability with increasing oxide thickness, and increase in the contact barrier height due to trapped positive charges in the oxide.<sup>[55]</sup> Modeling has shown that the oxide, being a back-contact barrier for holes, can account also for the rollover.<sup>[11, 54]</sup> Such a barrier can also explain the observed increase in series

resistance in the dark. The reason for the occurrence of crossover also under these stress conditions may well be the same as that given above for dark N<sub>2</sub> stressed cells. In addition it is possible that under illumination, at forward bias, the relatively thin CdTe (ca. 5 μm) allows a significant electron current to reach the back contact, thus increasing the total contact saturation current, which also can account for the cross-over (for discussion see <sup>[11, 56]</sup>).

Humidity is an important factor in air-induced degradation, as shown by the enhanced degradation during stressing in humid air, and by degradation of unstressed cells upon storage in humid air. Air and humidity together induce more severe degradation than is observed for each separately. Singh et al.<sup>[54]</sup> also showed that cells stressed at 100°C in dry air showed moderate degradation, while cells stressed at 100°C in high humidity showed significant degradation of all cell parameters with a rollover. Humidity was shown to increase the growth rate of CdTeO<sub>3</sub> on p-CdTe, when grown in wet oxygen, compared to growth in dry oxygen.<sup>[32]</sup> It is likely that, due to its polar and screening nature, H<sub>2</sub>O enhances oxidation by decreasing energy barrier(s) in the actual oxidation reaction. Therefore these observations support our model for the oxide at the CdTe back surface being the main culprit for air-induced degradation. Because the detrimental effect of humid air on the back contact is relatively fast, it needs to be avoided already from the very first stages after cell fabrication is completed. The small degradation observed in part of the cells stressed in dry N<sub>2</sub> in the dark can be explained by seasonal high humidity levels, adsorbed on the CdTe back surface and/ or in the graphite paste. Such humidity may facilitate the formation of a thin oxide layer at the back contact.

The stabilization of cells to degradation (by heat treatment in dry N<sub>2</sub> in the dark) that is normally observed with storage in room ambient, is thought to occur by the formation of the above-mentioned stable Cu<sub>2-x</sub>Te phase (x=0.015-0.026) at the back contact. This phase is expected to be less susceptible to air/humidity oxidation than a Te-rich CdTe surface. Further chemical analysis of the stability of Cu<sub>2-x</sub>Te to oxidation is needed to strengthen this hypothesis.

## 4. Conclusions

Chemical and electronic characterizations have been carried out on a series of cells which underwent a variety of thermal stress treatments, including monitoring effects of stress atmosphere, humidity and illumination on cell behavior. We postulate two independent mechanisms to explain degradation phenomena in heat stressed CdTe/ CdS solar cells (a schematic representation of all mechanisms is shown in figure 10):

### 4. 1. Cu doping of CdS

Cu is known to create acceptor states in CdS. Accumulation of Cu in the CdS with stress, together

with significant amounts of Cl (SIMS), increases the photoconductivity of CdS, and, hence, increases the dark resistivity of the material. Increasing photoconductivity of CdS (or other cell components) will NOT initially affect the illuminated J-V curve of a device, but will produce a significant increase in the degree of light-dark J-V crossover. Indeed, the stability of part of the cells stressed in dry-N<sub>2</sub> leads us to suggest that Cu-containing cells can be stable and that Cu is NOT a dominant factor in the initial degradation modes of these cells (as is also the case with Ag).

Excessive Cu doping of CdS can, however, be detrimental to cell performance. The acceleration of cell degradation by illumination during stress is explained by lowering of the electrostatic potential barrier to positively charged Cu ions crossing the cell junction, and, therefore, enhanced Cu accumulation in the CdS. Excess Cu may create deep acceptor states in the CdS, which can act as recombination centers and decrease the effective donor concentration. Compensation of donors in CdS was also used by Agostinelli et al.<sup>[57]</sup> as an explanation for degradation, in a model published recently. Recovery of light-stress induced degradation in CdTe/CdS cells by storage or anneal in the dark is explained by dissociation of the acceptor defects in CdS or in CdTe.

### 4. 2. Back contact barrier –

Oxidation of the CdTe back surface in O<sub>2</sub>/ H<sub>2</sub>O-containing environment to form an insulating oxide, by oxygen migration through the back contact, results in a back-contact barrier. This barrier is expressed by a rollover in the J-V curve. Humidity is an important factor in air-induced degradation, as it accelerates the oxide formation.

The back contact barrier may result from different factors, including depletion of Cu at the back contact/ CdTe interface, as is sometimes seen during light-induced degradation in inert atmosphere. However, regardless of the cause of the formation of the barrier at the back contact, this barrier is always expressed as rollover in the J-V characteristic.

*Heat treatment in the dark in inert atmosphere can stabilize the cells* against degradation induced by light stressing or by storage in humid air. This is explained by the completion of the contacting process, in which elemental Cu and Te are converted to the relatively stable Cu<sub>2-x</sub>Te (x=0.015-0.026). As a result, the release of Cu ions into the cell structure and the oxidation of the CdTe back surface are slowed, and cell degradation is noticeably attenuated.

## 5. Experimental

**Materials** To facilitate comparisons between results, we mainly discuss results obtained from cells, prepared from structures received from First Solar (FS), LLC (formerly Solar Cells, Inc.) without the back contact (cf. end of “*Stress Testing of Cells*”, below). In these structures the CdTe/CdS/transparent conductive

oxide (TCO)/glass structures were fabricated on 3 mm thick soda-lime glass, coated with 450 nm of TCO made of  $\text{SnO}_2\text{:F}$  (sheet resistivity  $8 \Omega/\square$ , Libby Owens Ford, TEC15 glass). Both the polycrystalline CdS and CdTe layers, 0.3 and 4  $\mu\text{m}$  thick, respectively, were deposited by closed space vapor transport. Unless specifically stated, all structures had received  $\text{CdCl}_2$ -vapor treatment at FS. Following  $\text{CdCl}_2$  treatment, the CdTe layers consisted of 1-2  $\mu\text{m}$  grains. Cells were prepared by applying a back contact (see below) on  $\sim 1 \times 1 \text{ cm}^2$  samples, cut from  $10 \times 10 \text{ cm}^2$  plates.

CdTe/TCO/glass structures, with the CdTe deposited by closed space sublimation and  $\text{CdCl}_2$ -vapor treated, were supplied by C. Ferekides (Univ. S. Florida).

**Back Contacts** Electrical contact to the CdTe back surface (the “back contact”) of most of the cells and structures used in this study were home-made, using HgTe:Cu doped graphite paste (Univ. S. Florida),<sup>[58]</sup> or graphite paste containing 0.4% w/w Cu powder (99.999%, Cerac). No difference in behavior between the two contact pastes was found. Due to this local back contacting procedure these devices need not be representative of standard, complete First Solar cells. Prior to back contact deposition, the samples were sonicated in water for 10 minutes to remove residual  $\text{CdCl}_2$ . The CdTe layers were then etched with 0.1% v/v  $\text{Br}_2$ /methanol for 10-20 seconds. The graphite paste was applied to an area of  $\sim 0.25 \text{ cm}^2$ , and annealed at  $250^\circ \text{C}$  for 25 minutes in a scrubbed (Oxiclear<sup>TM</sup> gas purifier)  $\text{N}_2$  atmosphere (typically  $<0.0001\% \text{ O}_2$  and  $<0.8 \text{ mg/l H}_2\text{O}$ ). For electrical measurements high purity Ag paint (SPI supplies) was applied to the back contact and, separately, to exposed TCO, and annealed at  $100^\circ \text{C}$  for 10 minutes in a scrubbed  $\text{N}_2$  atmosphere. To monitor behavior and diffusion of metallization species, a few cells were completed with Au metallization layer, deposited by evaporation of  $\sim 500 \text{ \AA}$  of Au (99.999 %) on the back contact, instead of Ag. Their initial performances and the behavior after stress were roughly comparable to that of the Ag-metallized cells.

Cells contacted in our laboratory, and subsequently used in further experiments, typically exhibit  $V_{oc} \sim 800 \text{ mV}$ ,  $J_{sc} \sim 20 \text{ mA cm}^{-2}$ , FF  $\sim 65\%$  and conversion efficiencies of 9-11% (see initial I-V curve in Figure 2). For re-contacting experiments, back contacts were removed by sonication in acetone. The freshly exposed CdTe surface was etched in 0.1% v/v solutions of  $\text{Br}_2$ /methanol or  $\text{Br}_2$ /ethylene glycol for 0 – 30s, prior to reapplication of the doped graphite paste and contact anneal as described before. Front and back contacts were again completed with Ag paste.

**Stress Testing of Cells** Thermal stressing of cells was carried out at  $200^\circ \text{C}$  at open circuit. The effects of different stress atmospheres were investigated: wet air (ambient room air), dry air (compressed air passed over two compartments containing  $\text{P}_2\text{O}_5$  desiccant), scrubbed dry  $\text{N}_2$ , and wet  $\text{N}_2$  (either dry  $\text{N}_2$  bubbled

through  $\text{H}_2\text{O}$  or sealed cell stress tube filled with dry  $\text{N}_2$ , connected to water reservoir). Stressing under illumination was done using a quartz-tungsten-halogen (QTH) projection lamp calibrated to AM 1.5 intensity ( $100 \text{ mW/cm}^2$ ). For some of the electrical measurements, cells were removed from stress conditions at various times and returned following the measurement. The overall number of cells stressed was about 120, with at least 7 cells stressed under each set of the stress conditions or stabilization processes (cf. <sup>[59]</sup>). We note that, for the sake of clarity, we have limited the cell results reported here to those obtained on cells made with structures from one and the same source. Qualitatively similar behaviour was observed in cells prepared from similar structures received from other sources. Still, the details of cell and back contact processing can affect the details of the cell response to stress (see <sup>[52]</sup> and references therein), even though the gross features reported here are observed for all.

**Characterization Methods** J-V measurements were carried out using a computerized, home-made set-up. Illuminated J-V's were recorded using a QTH projection lamp calibrated to AM 1.5 intensity ( $100 \text{ mW/cm}^2$ ).

LBIC measurements were obtained with an Olympus Fluoview scanning confocal microscope, employing an air-cooled Kr-Ar ion laser (568 nm) at 1 mW intensity. Cells were illuminated through the glass (as would occur for working devices in the field) beneath the back contact area. The laser-spot diameter was  $\sim 980 \text{ nm}$ , and the laser was rastered over an area of  $800 \times 600 \mu\text{m}^2$  at 3.2 s/scan. LBIC images were obtained using a homemade LBIC stage, with an Ithaco 1211 current amplifier, and Fluoview PC software. For the resultant front-wall LBIC images, the contrast represents the current scale, where white depicts areas of high current (corresponding to approximately  $10 \text{ A cm}^{-2}$ ) and black is no current.

For some characterization methods it was desirable to separate the contribution of different layers in the cell. To reach the CdTe directly, the back contact was removed by soaking in acetone in an ultrasonic bath. To sample the CdS directly the CdTe layer was removed by etching in 40% (w/w)  $\text{FeCl}_3(\text{aq})$ . Immediately upon complete dissolution of the CdTe layer, samples were immersed in  $\text{H}_2\text{O}$  and dried in a  $\text{N}_2$  stream. The completion of removal of CdTe was determined by the change in color of the sample. It is therefore possible that the etch process was stopped in the CdS/CdTe intermixed layer, introducing some uncertainty about the exact nature of the exposed surface after  $\text{FeCl}_3$  etch.

For SIMS analysis, back contacts were removed (as detailed above) and the cells etched in 0.1% v/v  $\text{Br}_2$ /methanol for  $\sim 30$  seconds, to remove the high Cu-containing layer at the surface, as such a layer can introduce measurement errors. Measurements were carried out using a 4 keV  $\text{O}_2^+$  beam in a Cameca IMS4f ion microscope. The primary beam was rastered over

an area of  $200 \times 200 \mu\text{m}^2$ , analyzing an area of  $60 \mu\text{m}$  in diameter. A mass resolution of  $M/\Delta M \sim 3000$  was required to avoid mass interferences. Due to the absence of implant standards, the conversion factors (RSF's) for species in the CdS, used for concentration calculations, were estimated using the systematic trend for positive ion yields vs. Impurity Ionization Potential.<sup>[60]</sup> All samples were measured by sputtering through the back (CdTe) side of the cells, and measurements were concluded upon reaching the TCO layer of the cell (determined from the Sn signal). Additional SIMS measurements were performed at NREL to detect possible lateral Cu diffusion out of the contact area. Depth profiles from the CdTe back surface were taken at designated locations under the (removed) contact or outside the contact area. Measurements at NREL were carried out using an  $\text{O}_2^+$  beam, with a spot size diameter of 2-3  $\mu\text{m}$ , profile current of 200 nA, imaging current of 1 nA, and a mass resolution of  $M/\Delta M \sim 4000$ .

AES of CdTe was performed using a 5600 Multi-Technique System (PHI). Measurements were obtained with an electron-beam of  $\leq 1 \mu\text{m}$  in diameter with energy of 10 keV and a target current of 10 nA. The sampled area was kept constant ( $10 \mu\text{m} \times 20 \mu\text{m}$ ) for all measurements.

XPS was carried out using an AXIS HS Kratos XPS/Auger surface analysis system using a  $\text{Al(K}\alpha\text{)}$  monochromated source (1486.6 eV). Depth profiling was made with Ar ion sputtering, with kinetic energy of 4 eV and emission current of 20 mA. Sputter rates varied between 40-70  $\text{\AA}/\text{min}$  (calibrated for  $\text{Ta}_2\text{O}_5/\text{Ta}$ ). Cd is known to be preferentially sputtered from CdTe, while Te is preferentially sputtered from  $\text{CdTeO}_3$ <sup>[32]</sup>.

PL measurements were carried out at 300 K employing the 514 nm line ( $\sim 50$  mW intensity) of an Ar laser and a standard PL setup equipped with 60 cm focal length double grating monochromator (Jobin-Yvon HRD) and cooled photomultiplier (Hamamatsu RG942) or liquid- $\text{N}_2$  cooled Ge IR detector. For CdTe/CdS samples, the CdS was excited through the glass at the cell front wall, while the CdS-only samples were measured directly.

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